Coordination Polymers with $[Au(CN)_4]^-$ Building Blocks: a 1-D Chain of Molecular $Ni^{II}_2Au^{III}_2$ Squares

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Abstract

A new coordination polymer utilizing the neglected cyanoaurate anion $[Au(CN)_4]^-$ building block is reported. Reaction of a Ni(II) salt, diethylenediamine (dien) and $K[Au(CN)_4]$ yields $Ni(dien)[Au(CN)_4]_2$, which consists of a unique bimetallic $Ni(II)_2/Au(III)_2$ supramolecular square through cis N(cyano) bridging of the $[Au(CN)_4]^-$ building block to $[Ni(dien)]^{2+}$ cations. These squares further aggregate into a 1-D chain via Au-N(cyano) interactions; no Au(III)-Au(III) interactions are observed. Within the square, the magnetic coupling between the Ni(II) centres is very weak, indicating that the $[Au(CN)_4]^-$ unit is a poor mediator of magnetic exchange in this system.

Introduction

The rational increase of structural dimensionality is an important synthetic goal in supramolecular systems. Such high-dimensionality systems may have useful non-linear optical, conducting, porous or magnetic properties.(1) Of particular interest to our group is the use of cyanometallate building blocks, due to their affinity to bridge transition metal centres and their generally predictable geometric and magnetic outcomes.(2) Specifically, we have extensively explored the linear $[Au(CN)_2]^-$ cyanometallate anion, which has the unique ability to form aurophilic interactions and is also luminescent, as a building block in supramolecular coordination polymers in an effort to utilize its special features to access unusual structural motifs and physical properties;(3) this work has recently been reviewed in Gold Bulletin.(4)

As a comparison with linear d^{10} $[Au(CN)_2]^-$, which forms aurophilic interactions, and square-planar d^8 $[Pt(CN)_4]^{2-}$, which forms Pt-Pt stacks,(5) we recently reported some of the first square-planar d^8 $[Au(CN)_4]^-$-based coordination polymers,(6,7) using the same transition-metal amine cations as for our dicyanoaurate and -argentate studies. Since some 1-D Pt-Pt chains can show strong conductivity, luminescence and electronic delocalization, it was considered important to determine if such properties could be accessed with isoelectronic Au(III). Unfortunately, to date no aurophilic Au(III)-Au(III) interactions or stacking have been observed in these systems; instead, Au-N(cyano) intermolecular contacts in the axial position of $[Au(CN)_4]^-$ were shown to dominate the supramolecular structures.

Nevertheless, the $[Au(CN)_4]^-$ building block is clearly capable of forming complexes and polymers by mono-coordination (through one N(cyano) donor), di-coordination in a cis or trans fashion and tetra-coordination, even though it is a weaker ligand than the Au(I) or Pt(II) counterparts.(6-8) Among these, cis-coordination generates an orthogonal bridging motif that would be expected to produce ferromagnetic interactions mediated by the $Au(CN)_4$-unit.(9) However, our previously reported examples with Cu(II) and cis-bridging $[Au(CN)_4]^-$ did not exhibit such interactions due to a Jahn-Teller distorted elongated bridging at the Cu(II) centre, which disrupted the potential magnetic interaction pathway.(6) This impediment could be avoided with the use of a Ni(II) centre (which does not generate Jahn-Teller distortion) in place of Cu(II), and we hereby report a chain of Ni(II)/$[Au(CN)_4]^-$ supramolecular squares containing the aforementioned *cis*-bridging binding motif, and its magnetic properties.

Results and Discussion

The aqueous reaction of the $[Ni(dien)]^{2+}$ cation (dien = diethylenetriamine) with two equivalents of an aqueous solution of $K[Au(CN)_4]$ produced a moderate yield of $Ni(dien)[Au(CN)_4]_2$ (1), which crystallized from the solution. The single-crystal X-ray structure of 1 is depicted in Figures

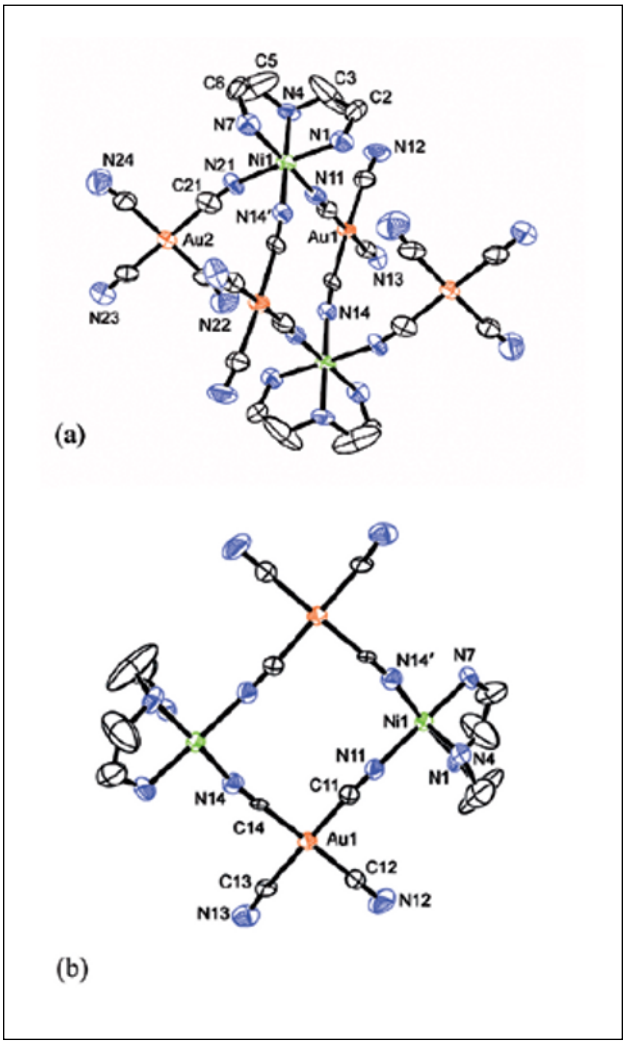

Figure 1

(a) Molecular structure of 1 (ORTEP view, 50% probability ellipsoids are shown; hydrogen atoms excluded for clarity). (b) Molecular structure of 1 with pendant $[Au(CN)_4]^-$ moieties omitted. Selected bond lengths (Å) and angles (deg): Ni1-N11 2.124(15), Ni1-N21 2.113(15), Ni1-N1 2.075(15), Ni1-N4 2.067(13), Ni1-N7 2.082(15) Ni1-N14′ 2.091(15); C11-Au1-C14 90.1(6), C21-Au2-C23 179.4(6), N11-Ni1-N21 85.0(6), N11-Ni1-N14′ 91.7(6), N11-Ni1-N7 170.1(6), N4-Ni1-N7 82.1(6), Ni1-N11-C11 169.6(15), Ni1-N14′-C14′ 163.1(14).′ = 3-x, -y, 2-z.

1 and 2.(10) As expected, the dien ligand occupies three facial coordination sites of the octahedral Ni(II) centre; the other three facially arranged coordination sites are filled with *N*-cyano ligands. Both $[Au(CN)_4]^-$ moieties are coordinated to the Ni(II) centre (Ni1–N11 = 2.124(15) Å and Ni1–N21 = 2.113(15) Å), however while one $[Au(CN)_4]^-$ unit is pendant (mono-coordinating), the other bridges to another Ni(II) centre (Ni1 – N14' = 2.091(15) Å) (Fig. 1) by utilizing cis-oriented *N*(cyano) donors. This produces a bimetallic square composed of two Ni(II) and two Au(III) centres (Fig. 1).

Despite the great interest in the preparation of molecular squares and cubes, which has focused on metals such as Re(I), Pt(II) and Pd(II),(11) the majority of such endeavours have utilized directing organic ligands to build the desired geometry. There are significantly fewer examples whereby metal complexes have been used as bridging moieties,(12) thereby producing the possibility

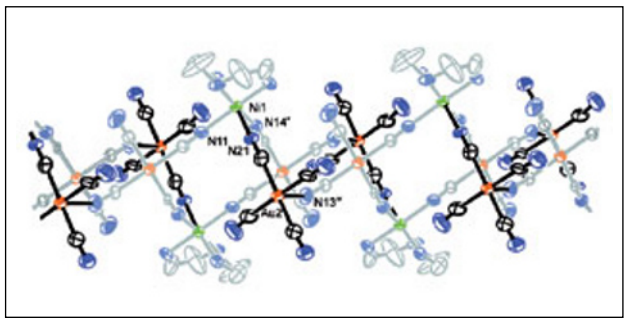

Figure 2

*Extended structure of **1** (ORTEP view, 50% probability ellipsoids are shown; hydrogen atoms excluded for clarity). Shaded portion is the molecular square depicted in Fig. 2(b). Selected bond lengths (Å) and angles (deg): Au2-N13″ 2.967(15).″ = x, y, z+1.*

of heterometallic systems.(13,14) Indeed, **1** qualifies as a heterometallic supramolecular square: both diagonal distances (Ni to Ni and Au to Au) within the square of **1** are approximately 7.3 Å. However, a van der Waals-based space-filling model of the structure (not shown) indicates that, although there is room for a very small molecule such as H_2 to enter the centre of the square, N_2 and other gases would not be likely to fit; this limitation is not due to the size of the square but to the pendant $[Au(CN)_4]^-$ units, which effectively block access to the central core for all but the smallest molecules and eliminate any 3-D channels that would otherwise exist. In accordance with this crystallographic data, no N_2 uptake was detected during a gas adsorption experiment. Similar heterometallic cyano-bridged squares to that of **1** have also been assembled using Fe(III)-CN moieties as building blocks.(14) Perhaps the most comparable structure is that of $[\{Cu(bipy)(H_2O)Pt(CN)_4\}_2] \cdot 2H_2O$, the first heterometallic square cyano-bridged complex with terminal cyano ligands, whereby the $[Pt(CN)_4]^{2-}$ moiety bridges in a *cis* fashion as well.(15) Interestingly, the discrete nature of this system was attributed to the presence of hydrogen bonding, preventing further coordination of the cyanometallate moiety.

Other intermolecular interactions are also present in **1**: adjacent bimetallic squares are connected through Au–N(cyano) interactions of 2.967(15) Å between the pendant Au2 and the N13-cyano donor, which is one of the two dangling cyanides of the *cis*-bridging $[Au(CN)_4]^-$ moiety. This generates a 1-D chain, which propagates perpendicular to the [100] axis (Fig. 2). Such Au(III)-N interactions were recently outlined for the first time; the Au-N distance in **1** is shorter than previously published examples, which range from 2.963(13) to 3.052(9) Å.(6,7) All of these distances are well below the sum of the van der Waals radii (3.27 Å).(16)

As was mentioned in the introduction, the $[Au(CN)_4]^-$ moiety is of particular interest as a magnetic mediator due to the inherent 90° angle that results from *cis* coordination. Thus, the temperature (T) dependence of the magnetic susceptibility (χ_M) of **1** was measured from 2-300K. For **1**, $\chi_M T$ = 1.1 cm^3 K mol^{-1} at 300 K per Ni(II) centre, as expected for independent Ni(II) atoms.(17) The $\chi_M T$ product is

temperature independent until 5 K, at which point it drops slightly to 1.0 cm^3 K mol^{-1} at 1.8 K, consistent with a small amount of zero-field splitting (D) at low temperatures and possibly a very weak ferromagnetic interaction (J) overlaid; modelling this data was not considered to be worthwhile in terms of yielding meaningful D or J-parameters (both are very small).(18) Thus, this data suggests that the two Ni(II) centres act essentially independently of each other despite the presence of the cis-coordinate bonded NC-Au(III)-CN interaction pathway; in other words, the $[Au(CN)_4]^-$ unit in **1** is a surprisingly poor mediator of magnetic exchange in this system, likely worse than the related $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ moieties.(19) For reference, other Ni(II) dimers with cyanato, thiocyanato and selenocyanato bridging have shown magnetic coupling J values ranging from −4.4 cm^{-1} to 2.4 cm^{-1}.(20)

Conclusions and Future Prospects

It has become clear that $[Au(CN)_4]^-$ is a viable building block with which to form heterometallic coordination polymers, although it forms materials that are not as strongly held together as for $[Au(CN)_2]$-based systems; the square-planar gold(III) analogue also does not exhibit any aurophilic interactions. Instead, gold-*N*(cyano) interactions dominate the intermolecular packing arrangement. Issues of structural control that result from the weaker Au(III)-*N*(cyano) binding to transition-metals can be compensated for by utilizing more inert, Jahn-Teller-free metals such as Ni(II); in this contribution a $Ni(II)_2Au(III)_2$ supramolecular square was assembled. More research should yield information on how to predict and control the nature of the structures produced, given a specific metal/ligand combination. In particular, the potential conductivity of $[Au(CN)_4]^-$ stacks (as yet unobserved) and the potentially hemilabile nature of the cyanoaurate(III) *N*(cyano) binding both provide impetus for a further exploration of $[Au(CN)_4]^-$-based coordination polymers, although significant magnetic coupling is not likely to be observed in these systems. The use of cyanoaurates as components of advanced materials would provide a new utility and market for these key compounds of the gold mining and refining industry.

Experimental

General Procedures and Materials: All reagents were purchased from commercial sources and used as received. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer with samples prepared as KBr pressed pellets. Microanalyses (C, H, N) were performed by Mr. Miki Yang using a computer-controlled Carlo Erba (Model 1106) CHN analyzer.

Magnetization measurements were performed with a Quantum Design MPMS-XL-7S SQUID magnetometer with an Evercool-equipped liquid helium dewar. A microcrystalline sample of **1** was packed in a gelatin capsule and mounted in a diamagnetic plastic straw. Direct current (dc) magnetization was measured upon cooling from 300 to 1.8 K under applied dc fields of 10 kOe and 1000 Oe; no field dependency was observed. The magnetic susceptibility of **1** was corrected for the diamagnetic contribution of the constituent atoms using Pascal's constants.(9)

*Synthesis of **1**:* To a 5 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.055 g, 0.189 mmol) was added a 1 mL aqueous stock solution (0.189 mmol) of diethylenetriamine (dien). While stirring, a 5 mL aqueous solution of $KAu(CN)_4$ (0.128 g, 0.377 mmol) was added drop-wise to this pale purple solution. The resulting solution was covered and left undisturbed. After one day, 36 mg of pale purple X-ray quality crystals of $Ni(dien)[Au(CN)_4]_2$ (**1**) were deposited from the solution. Over several weeks, more crystals and crystalline powder were deposited from the solution. Total yield: 0.077 g (53%). Anal. Calcd for $C_{12}H_{13}N_{11}Au_2Ni$: C, 18.87; H, 1.72 ; N, 20.17. Found: C, 18.99; H, 1.71; N, 19.94. IR (KBr): 2236 (υCN), 2231 (υCN), 2199 (υCN), 2187 (υCN), 3353, 3327, 3306, 1611, 1077, 1037, 1006, 981, 660, 567, 431, 423 cm^{-1}.

X-ray Crystallography. A single crystal of **1** was mounted on a glass fiber using epoxy adhesive. Single crystal X-ray diffraction data was recorded between $4° < 2\theta < 48°$ on an Enraf Nonius CAD4F diffractometer equipped with a Mo K_α source (λ = 0.71073 Å) and controlled by the DIFRAC program.(21) The NRCVAX Crystal Structure System was used to perform a psi-scan absorption correction (in the transmission range 0.0724-0.156) and data reduction, including Lorentz and polarization corrections. The crystal structure was solved using the Sir 92 routine and refined through Fourier techniques using the CRYSTALS software package;(22) crystallographic data for **1** are summarized in reference 10. All non-hydrogen atoms were refined anisotropically. Full matrix least-squares refinement (1933 reflections included) on *F* (232 parameters, 12 restraints) converged to R_1 = 0.0411, wR_2 = 0.0494 ($I_o > 2.5\sigma(I_o)$). Hydrogen atoms were placed in geometric positions and their coordinates allowed to ride with their associated atoms. Full details of the crystal structure data, solution and refinement have been deposited in CIF format with the Cambridge Structural Database and can be retrieved by citing the reference number CCDC-622240.

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About the Authors

Dr. Daniel Leznoff completed his Ph.D. degree with Professor Michael Fryzuk in 1997 at the University of British Columbia (Vancouver, Canada). He was an NSERC Postdoctoral Fellow from 1997-1999 at the Bordeaux Institute for Condensed Matter Chemistry (ICMCB-CNRS) under the supervision of Professor Olivier Kahn. In 1999 he joined the Chemistry Department at Simon Fraser University (Burnaby, Canada), where he is now Associate Professor. His interests include the synthesis and characterization of gold and silver-containing heterometallic coordination polymers for materials applications, paramagnetic organometallic chemistry and actinide chemistry.

Ms. Carolyn Shorrock completed an M.Sc. thesis in the Leznoff group on cyano-gold(III) and -silver(I) coordination polymers in 2003 and is currently a Chemistry Lecturer at Langara College (Vancouver, Canada).

Dr. Raymond Batchelor is a Senior Lecturer at Simon Fraser University responsible for computer-assisted learning; he also spent many years as a crystallographer in conjunction with Prof. Frederick Einstein (SFU).

References

1 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2003, 2781 and references therein; L. Ouahab, *Chem. Mater.*, 1997, **9**, 1909

2 J. Lefebvre, D.B. Leznoff, *Chapter 7* in: *Macromolecules Containing Metal and Metal-Like Elements*, A.S. Abd-El-Aziz, C.E. Carraher Jr., C.U. Pittman Jr., M. Zeldin, (Eds), Wiley-Interscience, 2005, **6**, 155; M. Ohba, H. Okawa, Coord. *Chem. Rev.*, 2000, **198**, 313; K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283; T. Iwamoto, in *Comprehensive Supramolecular Chemistry*, J. M. Lehn, J. L. Atwood, J. E. D. Davie, D. D. MacNicol, F. Vogtle, G. T. B. Alberti, Eds. Pergamon Press: Oxford, 1996, Vol. 7 pp 643-690 and references therein

3 D. B. Leznoff, B.-Y. Xue, B. O. Patrick, V. Sanchez and R. C. Thompson, *J. Chem. Soc., Chem. Commun.* 2001, 259; D.B. Leznoff, B.-Y.Xue, C. L. Stevens, A. Storr, R. C. Thompson and B. O. Patrick, *Polyhedron*, 2001, **20**, 1247; D.B. Leznoff, B.-Y. Xue, R. J. Batchelor, F. W. B. Einstein and B. O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026; J. Lefebvre, R. J. Batchelor and D. B. Leznoff, *J. Am. Chem. Soc.*, 2004, **126**, 16117; M. J. Katz, P. M. Aguiar, R. J. Batchelor, A. Bokov, Z.-G. Ye, S. Kroeker, D. B. Leznoff, *J. Am. Chem. Soc.*, 2006, **128**, 3669; J. Lefebvre, F. Callaghan, M. J. Katz, J. E. Sonier, D. B. Leznoff, *Chem. Eur. J.*, 2006, **12**, 6748

4 D. B. Leznoff, J. Lefebvre, *Gold Bull.*, 2005, **38**, 47

5 D. M. Roundhill, In *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard, J. A. McCleverty Eds., Pergamon Press: Oxford, 1987, **5**, 351; I. Escorihuela, L. R. Falvello, M. Tomás, *Inorg. Chem.*, 2001, **40**, 636; K. Sakai, E. Ishigami, Y. Konno, T. Kajiwara, T. Ito, *J. Am. Chem.* Soc., 2002, **124**, 12088

6 C. J. Shorrock, H. Jong, R. J. Batchelor and D. B. Leznoff, *Inorg. Chem*, 2003, **42**, 3917

7 M. J. Katz, C. J. Shorrock, R. J. Batchelor, D. B. Leznoff, *Inorg. Chem.*, 2006, **45**, 1757

8 P. Vitoria, I. Muga, J.M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, F.J. Zúniga, J.I. Beitia, I*norg. Chem.*, 2003, **42**, 960;

9 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993

10 *Crystal Data for 1*: $C_{12}H_{13}N_{11}Au_2Ni$, M = 763.94, monoclinic, space group $P2_1/n$, a = 9.9807(14), b = 19.811(2), c = 10.300(2) Å, β = 100.364(11)°, V = 2003.4 Å^3, Z = 4, μ(Mo-Kα) = 155 cm^{-1}, T = 273 K, 3165 unique reflections, 1933 observed ($I_0 > 2.5\sigma(I_0)$). The final $R(F)$ = 0.0411 and $wR(F)$ = 0.0494 (observed data). See CCDC-622240 for full details

11 D. A. Beauchamp, S. J. Loeb, *Chem. Commun.* 2002, 2484; B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* 2001, **40**, 2022 and references therein; C. J. Kuehl, S. D. Huang, P. J. Stang, *J. Am. Chem. Soc.* ,2001, **123**, 9634.; S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* 2000, **100**, 853; S. Bélanger, M. H. Keefe, J. L. Welch, J. T. Hupp, *Coord. Chem. Rev.* 1999, **190-192**, 29; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; D. H. Cao, H. Chen, J. Fan, J. Manna, B. Olenyuk, J. A. Whiteford, P. J. Stang, *Pure Appl. Chem.* 1997, **69**, 1979

12 S.-S. Sun, A. S. Silva, I. M. Brian, A. J. Lees, *Inorg. Chem.*, 2000, **39**, 1344 and references therein

13 C. P. Berlinguette, J. R. Galán-Mascarós, K. R. Dunbar, *Inorg. Chem.*, 2003, **42**, 3416

14 H. Oshio, M. Yamamoto, T. Ito, *Inorg. Chem.*, 2002, **41**, 5817; J. K. Bera, B. W. Smucker, R. A. Walton, K. R. Dunbar, *Chem. Commun.*, 2001, 2562; H. Oshio, H. Onodera, O. Tamada, H. Mizutani, T. Hikichi, T. Ito, *Chem. Eur. J.*, 2000, **6**, 2523

15 L. R. Falvello, M. Tomás, *Chem. Commun.* 1999, 273

16 A. Bondi, *Phys. Chem.*, 1964, **68**, 441

17 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, 1986

18 Magnetic properties of selected Ni(II) dimers: S. Deoghoria, S. Sain, M. Soler, W. T. Wong, G. Christou, S. K. Bera, S. K. Chandra, *Polyhedron*, 2003, **22**, 257; E. Ruiz, J. Cano, S. Alvarej, P. Alemany, *J. Am. Chem. Soc.*, 1998, **120**, 11122; G. A. van Albada, J. J. A. Kolnaar, W. J. J. Smeets, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.*, 1998, 1337; M. G. Barandika, R. Cortéz, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 2971; R. J. Butcher, C. J. O'Connor, E. Sinn, *Inorg. Chem.* 1981, **20**, 3486; A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* 1972, **11**, 2884

19 C. J. Shorrock, B.-Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick, D. B. Leznoff, *Inorg. Chem.*, 2002, **41**, 6743

20 D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* 1974, **13**, 2929

21 E.J. Gabe, P.S. White, G.D. Enright, *DIFRAC A Fortran 77 Control Routine for 4-Circle Diffractometers*, N.R.C., Ottawa 1995

22 P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *J. Appl. Crystallogr.* 2003, **36**, 1487